Recent directions of world hydrogen production

M. Momirlan[a],*, T. Veziroğlu[b]

[a] *Institute of Physical Chemistry "I.G. Murgulescu", Romanian Academy, Spl. Independentei 202, Bucharest 77208, Romania*
[b] *Clean Energy Res. Inst., University of Miami, Coral Gables, FL 33124, U.S.A.*

Abstract

Hydrogen can be produced on a large scale through economically favorable raw materials and processes. Utilization of water as an exhaustible supply of hydrogen is well known. This is very much an area open to research, so that traditional methods can be considered, as well as non-traditional approaches. This paper examines the present status and looks at different approaches for technological advances. The paper reports on some of the new developments in the progress of the recent directions of world hydrogen production, with emphasis on photolytical hydrogen processes. The aim of this article is to inform the reader of new research on hydrogen production. © 1999 Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

Fossil fuels possess very useful properties not shared by non-conventional energy sources (such as solar) that have made them popular during the last century. Unfortunately, fossil fuels are not renewable [1]. In addition, the pollutants emitted by fossil energy systems (e.g. CO, CO_2, C_nH_m, SO_x, NO_x, radioactivity, heavy metals, ashes, etc.) are greater and more damaging than those that might be produced by a renewable based hydrogen energy system [2]. Since the oil crisis of 1973, considerable progress has been made in the search for alternative energy sources. Although the water splitting process used to simultaneously generate hydrogen and oxygen has been demonstrated by the utilization of insolation, the technology is not mature enough to bring it to demonstration level. Much fundamental research remains to be done [3]. A long sought goal of energy research has been the search for a method to produce

---

* Corresponding author. Tel.: 00 401 725 5857; e-mail: mmagdalena@chimfiz.icf.ro

hydrogen fuel economically by splitting water using sunlight as the primary energy source.

One of the main domains of solar energy research concerns the development of a process for the production of 'solar fuels'. Among the solar fuel candidates, hydrogen holds a pre-eminent position because of its high energy content, environmental compatibility and ease of storage and distribution.

The different approaches for splitting water have been summarized by Bockris as follows: electrolysis, plasmolysis, magnetolysis, thermal approach (direct, catalytic and cyclic decomposition of water, as well as magmalysis), use of light (photosensitized decomposition using dyes, plasma-induced photolysis, photoelectrolysis, photo-aided electrolysis, the indirect path towards hydrogen by photoelectrolysis: the photo-electrochemical reduction of CO_2 and photovoltaic electrolysis), biocatalytic decomposition of water, radiolysis and other approaches [4].

Worldwide production of CO_2 emission to reduce the risk of climate change (greenhouse effect) requires a major restructuring of the energy system. The use of hydrogen as an energy carrier is a long term option to reduce CO_2 emissions. However, at the present time, hydrogen is not competitive with other energy carriers. The production costs of hydrogen from CO_2-free electricity (hydro, nuclear and solar) are typically 20–30 Ecu GJ^{-1} or more, which does not compare with today's oil and gas prices of 5 Ecu GJ^{-1}. Fossil fuel conversion to hydrogen, with separation and storage of CO_2, might be an attractive transitional CO_2-free source of hydrogen at costs of 10–15 Ecu GJ^{-1}. A scenario study has been reported incorporating a complete set of new technologies (including hydrogen production) to reduce CO_2 emissions by the year 2040 [5].

Global utilization of fossil fuels for energy needs is rapidly resulting in critical environmental problems throughout the world. Energy, economic and political crises, as well as the health of humans, animals and plant life, are all critical concerns. There is an urgent need to expedite the process of implementing the Hydrogen Economy. A worldwide conversion from fossil fuels to hydrogen would eliminate many of the problems and their ramifications. The optimal endpoint for conversion to the Hydrogen Economy is the substitution of clean hydrogen for the present fossil fuels. The production of hydrogen from non-polluting sources (such as solar energy) is the ideal way [6]. Many environmental advantages can thrive within the Hydrogen Economy, and as such, it can be referred to as the Hydrogen Environmental Economy.

The utilization of solar quantum and thermal photons seems to be significant in the future work on hydrogen production. Solar hydrogen is not an energy, but a chemical energy carrier that enables worldwide loss-free storage and low-loss transportation of macro-economically relevant quantities of the secondary energies, heat or electricity. These can be generated from solar energy, albeit from solar irradiance, wind, hydropower, or ocean temperature gradients, or by using the two non-solar renewable energy sources, i.e. the motion of the tides and the heat of the Earth's magma. Solar hydrogen makes it possible for solar energy to be traded on the world's energy market. This market can thus be perpetuated beyond that point in time when the fluid hydrocarbons remaining in the Earth's crust will no longer be available

for energetic utilization. The status of research, development and demonstration of energetic solar hydrogen systems and their components were presented, including both scientific and technical aspects.

The amount of solar energy reaching the Earth is enough to supply mankind with many thousand times the energy it presently requires. This energy supply is, however, neither constantly available nor distributed equally over the surface of the globe. Indeed, the places where mankind's energy consumption is highest are not the places where the Sun's irradiance is at a maximum. If the Sun's daytime energy supply also has to be used at night, or its summer supply also in the winter, if the solar energy available at places with high insolation is also needed at places with low insolation and large energy demands, then it is physically impossible to meet these needs directly with the primary energy of solar irradiance.

Solar hydrogen is a clean energy carrier. Electrolytic hydrogen is made from water and becomes water again. Hydrogen obtained from solar energy (solar hydrogen) is ecologically responsible along its entire energy conversion chain. At only one link of the chain can a pollutant, nitrogen oxide, arise; and this occurs only if the hydrogen is not recombined with pure oxygen, but using air as an oxidant, such as in reciprocating piston engines or gas turbines on board automobiles or aircraft. At the high reaction temperatures which arise in such places, the oxygen and nitrogen in the air can combine to form nitrogen oxide.

Solar energy stored in hydrogen is available at any time and at any place on Earth, regardless of when or where the solar irradiance (or the hydropower, biomass, ocean energy or wind energy) was converted. The fundamental discrepancies in the times and places of solar energy supply and human energy demands can be overcome using hydrogen. Solar hydrogen makes solar energy as storable and transportable as oil and natural gas are by nature, but without the burden of their negative environmental impact. Solar hydrogen combines the advantages of hydrocarbons (storability and transportability) with the advantages of solar energy (ecological acceptability, renewability and low risk). Solar hydrogen has no need for the carbon atom, which makes the hydrocarbons almost infinitely storable at room temperatures, but is also the reason for their negative ecological impact. Solar hydrogen provides the link between the pre-industrial solar era, the first solar civilization, which only knew of stored solar energy in the forms of biomass and hydropower, and a post-fossil fuel era, the second solar civilization [7–8].

Hydrogen is a carbon-free fuel which oxidizes to water as a combustion product. The generated water becomes, together with renewable primary energy for splitting it, a source of clean and abundant energy in a carbon-free, natural cycle [9].

In the development of all new energy options, hydrogen necessarily will play an important role because of its ability to supplement any energy stream and applied to any load. Hydrogen will act as a solar storage medium and transform solar energy into a transportation fuel [10].

Recently, four solar hydrogen systems have been selected as showing sufficient promise for further research and development: (1) photovoltaic cells plus an electrolyzer, (2) photoelectrochemical cells with one or more semiconductor electrodes, (3) photobiological systems and (4) photodegradation systems [11].

2. Main approaches for hydrogen production

Much of the hydrogen produced in the world, and especially for the petrochemical industry, is obtained from natural gas, which is mostly made up of methane. The bulk production of hydrogen is through the catalyzed steam reformation of methane. However, the uncatalyzed partial oxidation of methane for appropriate optimization may be used to produce hydrogen at very attractive overall cost and energy efficiency. The combustion of rich mixtures of methane representing natural gas in air or oxygenated air involving the uncatalyzed partial oxidation of methane can be examined analytically. A detailed chemical kinetic scheme made up of 108 simultaneous reaction steps with 28 reactive species has been evaluated [12].

Water electrolysis is one of the most utilized industrial processes for hydrogen production today. The three major technologies currently under consideration for electrolytic hydrogen production are alkaline, polymer membrane and ceramic oxide electrolyte. Direct conversion of solar energy into hydrogen as a storable energy source can be achieved theoretically by photoelectrochemistry. The utilization of solar quantum and thermal photons is important for technological progress, particularly for the high-temperature thermochemical and photochemical fields. Although the water splitting process to generate hydrogen and oxygen simultaneously has been reported by the utilization of light energy, it is not mature enough for pilot plant demonstrations. Much of the fundamental research remains to be done. Among the different approaches, photocatalysis has received much attention as a possible method for photochemical conversion and storage of solar energy. Photosynthetic bacteria represent a method with appreciable extent efficiency for hydrogen evolution using solar energy.

Certain hydrogen production processes have reached maturity for commercial exploitation: (a) steam reforming of natural gas; (b) catalytic decomposition of natural gas; (c) partial oxidation of heavy oils; (d) coal gasification and (e) steam-iron coal gasification. Other processes, such as thermochemical, photochemical, photoelectrochemical and photobiological processes are being explored or already at the research and development stage. The main processes for hydrogen production and their status of development are summarized in Table 1.

2.1. *Electrochemical processes*

Water electrolysis is one of the most important industrial processes for hydrogen production today, and is expected to become even more important in the future. The three major technologies currently under consideration for electrolytic hydrogen production are classified as alkaline, polymer membrane and ceramic oxide electrolyte. Development of solid electrolytes for water electrolysis at intermediate temperatures is important [14].

Critical to the electrochemical situation is the work of Kainthla et al. who carried out calculations that gave rise to the theory of how two photovoltaics could be coupled together [15]. It was shown that the relation of their energy gap to the flatband

Table 1
Summary of main hydrogen production processes [13]

Production process	Status
Steam reforming of natural gas	Mature
Catalytic decomposition of natural gas	Mature
Partial oxidation of heavy oil	Mature
Coal gasification	R & D—Mature
Steam-iron coal gasification	R & D
Water electrolysis	Mature
Thermochemical cycles (pure)	R & D
Thermochemical cycles (hybrid)	R & D
Photochemical processes	Early R & D
Photoelectrochemical processes	Early R & D
Photobiological processes	Early R & D

potential was critical. The substances which the theory indicates are suitable (non-oxides) would form oxides upon the evolution of oxygen, so that it was necessary to coat them with a non-permeable coating.

A principal focus of modern research in hydrogen production by electrolysis is to discover electrode materials that exhibit good electrochemical stability and show interesting activity for the typical electrochemical reactions. It is also desirable that these materials be inexpensive, abundantly available, easy to manipulate and non-polluting. Such a class of materials is represented by metal silicides [16].

The current-voltage behavior of hydrogen evolving Raney-nickel electrodes has been extensively explored [17]. Raney-nickel cathodes prepared by different methods are increasingly applied in the most important electrochemical technologies. The effectiveness in enhancing the catalytic activity of nickel electrodes by employing three types of particulate materials, namely Raney-nickel, aluminium and alumina powders during the cathodic codeposition of nickel has been researched [18].

Hydrogen evolution reaction mechanism on electrodeposited Ni–S coatings of low sulfur content was initially studied in alkaline solutions through steady-state polarization measurements. Tafel plots have been analyzed at several temperatures and varying pH values. The results suggested a mechanism involving fast electron transfer followed by a slow electrochemical desorption step [19]. The hydrogen evolution in the basic medium of iron or nickel electrodeposited with heteropolyacids has been investigated [20].

Solid polymer electrolyte technology, i.e. proton exchange membrane technology in which the two electrodes are coated or pressed onto a membrane used as the electrolyte, is the most promising candidate for low temperature fuel cells [21].

In order to create a CO_2 neutral, regenerative energy system based on methanol, a new coupled process has been proposed through the production of hydrogen by water electrolysis and CO_2 from the atmosphere [22].

2.2. *Thermochemical processes*

More than 200 thermochemical cycles have been reported, but the technical status of many of them is at the experimental or bench-scale stage. The main reason for this is the technical problems to be solved before commercialization, such as the separation of products and the circulating agent and equipment development for industrialization. In addition, thermochemical reactions may cause pollution problems if the process is not completely closed.

A search program which uses only the free energies of formation has been developed to find new thermochemical cycles for the production of hydrogen from water. Some representative closed cycles mainly composed of copper compounds with three-step reactions have been presented. The KIER-3 cycle using copper oxide and copper sulfate seems to be the most practical one among them [23]. Thermochemical water splitting cycles through direct HI decomposition from H_2O–HI–I_2 solutions and the results for different concentrations and temperatures up to 220°C have been reported [24]. A number of potential thermochemical water splitting processes have been evaluated quantitatively by computer model evaluations.

The redox systems studied, which could achieve decomposition of water in two steps by condensed redox phases, were the oxide systems $CoO(Co_3O_4, MnO/Mn_3O_4, FeO/Fe_3O_4, NbO_2/Nb_2O_5)$ and the halide systems FeX_2/Fe_3O_4, where $X = $ F, Cl, Br or I. The results from the calculations have been utilized to outline the conditions for hydrogen production and possible deoxidization and reformation subprocesses [25].

Ceramic-based support materials are of interest for hydrogen production through the UT-3 thermochemical water-decomposition cycle [26–28]. The UT-3 thermochemical water-decomposition cycle requires Fe reactant pellets with high activity and long life. Properties of Fe reactant pellets using ZrO_2–$Y_2O_3, ZrSiO_2 + ZrO_2$ as support materials have been evaluated [29].

Recently new data on yields of hydrogen iodide from oxidation of dehydrated disulfide monosulfate 4-hydrate, admixed with a cerium dioxide substrate, were reported. Some of these data have been used for evaluation or modification of the sulfur dioxide-iodine thermochemical cycle for hydrogen production [30].

A new two-step thermochemical cycle for hydrogen production has been suggested and the main reactants, Cr_2O_3 and *M*OH (*M* = K, Na, Ba or Mg), have been tested [31].

A thermocatalytic process for hydrogen generation has been developed using water in the presence of zeolite catalysts impregnated with non-noble metals of variable valences and activated in vacuum [32]. For optimizing the technological flow, continuous decomposition of water in reaction-regeneration catalyst cycles in moderate vacuum at temperatures up to 500°C has been achieved [33]. Two methods for the activation of zeolites have been established: (1) vacuum outgasing at temperatures ranging between 300 and 500°C, and (2) activation of zeolites with UV and UV-IR radiation. An electronic microbalance (10^{-6} g) has been used for measurements of weight variations of zeolites during their activation. The activation–deactivation curves have been generated. An experimental device has been built for the catalytic

decomposition of water over zeolites with the capability of measuring mass variation of zeolites during irradiation [34].

A reactor has been built to study the hydrolysis of $FeCl_2$ for the hydrogen generation step in the thermochemical cycles from the Fe-Cl family. Equipment for high temperature kinetic studies on gas–solid heterogeneous reactions have been described. The preliminary test results and some problems generated by the use of anhydrous $FeCl_2$ as solid phase and corrosive character of the gaseous phase, due to the presence of HCl have been presented [35]. The criteria for the selection of the thermochemical cycles used to establish the maximum efficiency for multi-step water splitting have been analyzed. A model for performing the selection of thermochemical water splitting cycles has been presented. The steps for having a negative contribution to the overall thermal efficiency have been identified [36].

2.3. Photochemical processes

Considerable attention has been given to the process of splitting water into hydrogen and oxygen with the use of sunlight, because it could result in a low-cost method of producing hydrogen [37]. As is well known, the spatial distribution of solar radiation may be strongly non-uniform. Indeed, the amount of solar radiation at ground level depends on the latitude and some other factors, such as the altitude and the atmospheric conditions. Consequently, studies concerning the meteoro-climatological features of a given site must be considered before designing a solar installation there. In order to estimate the availability of solar global radiation, the Angstrom–Page formula can be used. The relationship predicts the value of relative sunshine (the ratio between the hours of bright sunshine and the daily light hours) [38].

One of the possibilities of hydrogen production by solar energy is the direct photochemical reduction of water. A sensitizer is excited by visible light and can thereafter affect redox reactions, yielding electrons for the water reduction. One of the benefits of this system is that several sensitizers with different absorption characteristics can be used simultaneously, leading to higher quantum yields per unit area. The ground and excited states of sensitizers differ significantly in the redox potentials. Usually, the more electronegatively excited sensitizers deliver the needed electrons for the water reduction.

For the photochemical reduction of water, a catalyst is usually needed, and in most cases, a heterogeneous noble metal catalyst is used. These metals are generally present as small particles, and to impede precipitation a protective agent (usually a polymer) is added, which reduces the catalytic activity. With such catalysts, it is difficult to obtain reproducible results, since diminutive variations in the synthesis may result in considerable deviations in the activity of the catalyst. The aging of the catalysts is also important.

Systems using colloidal noble metals as catalysts need a separate electron relay compound. One of the main problems with such electron relay compounds is the hydrogenation of their double bonds, and that their reduced forms (radicals) are often very reactive towards oxygen.

A better choice would be a homogeneous catalyst with high catalytic activity, and hence no precipitation problem. Further, with a homogeneous catalyst, a better distribution around the sensitizer molecules can be obtained. Various enzymes have been tested as water reduction catalysts, but none of them has worked efficiently. A homogeneous water soluble Wilkinson's catalyst has been investigated by Oishi, and showed excellent catalytic activity for water reduction. This substance combines the features of an electron relay compound and a catalyst that exists in different redox states [39].

It has been confirmed that the bifunctional redox catalyst $Pt/Bi_2O_3/RuO_2$ mediates photocleavage of water in the presence of MV^{2+} on irradiation with visible light of $\lambda > 410$ nm in the presence of $Ru(bpy)_3^{2+}$ with a light of $\lambda > 450$ nm [40].

A common problem in reactor design is the determination of the extensive reaction rate as a function of the intensive rate, the flow model and the geometry of the system. For a photoreactor, the issue is complicated by the fact that the rate depends on the distribution of radiation on it. The determination of this light distribution is very complex for the heterogeneous catalytic systems. This problem has been undertaken for tubular reactors with photocatalytic membranes supported on spheres or concentric cylinders. Computer simulation programs based on the Monte Carlo method have been developed for the case. The influence of several variables, such as the absorbency of the catalyst and the support, the refraction indexes and the diameter of the spheres, has been studied. The radiation absorption efficiencies of different systems of supporting the photocatalytic membranes have been compared, and design equations based on simulation results have been proposed [41].

The photophysics and photochemistry of the adsorbed layer remained one of the most unexplored fields in photochemistry for a long time, when compared with studies in homogeneous systems. Recently, studies of the photophysics and photochemistry of molecules adsorbed on inert adsorbents, such as SiO_2 and zeolites, have received a great deal of attention from the standpoint of photochemical processes on solid surfaces, providing a new research field, namely 'heterogeneous photochemistry'. In addition to these, however, more recent studies of surface photochemistry have been given a great deal of attention due to their potential for yielding a promising number of useful applications including the control of photochemical reaction paths and conversion of light energy to useful chemical energy.

In connection with the problem of adsorption and catalysis, a number of studies were carried out in the field of photocatalysis, which were initially concerned with the effect of irradiation of the catalysts in their fundamental adsorption bands on their catalytic activities and selectivities for catalytic reactions. In this case, the reactant molecules usually show no absorption in the absorption regions of the catalyst. Instead of activating a solid catalyst by irradiation, however, it seems possible that a reactant or an intermediate complex formed on the surfaces is activated by irradiation, which results in acceleration of the reaction or the occurrence of a new reaction. Recently, this field has been expanding rapidly in connection with light energy, especially in the conversion of solar energy to chemical energy using solid catalysts such as TiO_2 [42].

2.4. *Photocatalytical processes*

Solar utilization via chemical storage can be achieved by photocatalytic and/or photoelectrochemical activation of light sensitive semiconductor surfaces. The absorption of photons corresponding to the fundamental absorption band of the catalyst leads to the formation of electron-hole pairs, some of which undergo radiative decay as photoluminescence. Therefore the studies of photoluminescence (PL) in the presence of reactant molecules are expected to be useful not only in understanding the surface structure and the excited states of the catalysts, but also as a probe for surface processes leading to the photochemical production of electrons and holes. However, although TiO_2 catalysts are known to exhibit high activity for decomposition of H_2O, few PL studies have been carried out in connection with photocatalysis and/or photoconductance. The addition of unsaturated hydrocarbons onto the TiO_2 catalyst causes an increase in intensity of PL of the catalyst as a radiative surface process from photoformed electrons and holes. The extent of the PL enhancement strongly depends on the ionization potential of the added compounds, i.e., the lower the ionization potential of the added compound, the larger the PL intensity. A parallel relationship between the enhancement of the TiO_2 by the addition of the unsaturated hydrocarbons and the rate of photocatalytic hydrogenation of these compounds with H_2O on the TiO_2 catalysts, suggests that these surface processes are closely associated on binding of the added molecules to the TiO_2 surface [43]. The influence of altervalent cation doping of TiO_2 on its performance as a photocatalyst in water cleavage has been investigated. It has been shown that under illumination in the near-UV region, platinized anatase exhibits hydrogen production rates which are significantly higher than those of the rutile form [44].

Superoxide (O^{2-}) has been shown to be readily generated in aqueous solutions with vacuum-UV lamps of simple design. A mechanism has been proposed and shown to account for the results by comparison to computer calculations [45].

Photocatalytic decomposition of water into hydrogen and oxygen using semiconductors loaded with various metals have been widely studied [46]. An addition of Na_2CO_3 played an excellent role for the stoichiometric photodecomposition of liquid water over TiO_2 and $SrTiO_3$ loaded with various metals such as Pt, RuO_2 and NiO_x [47].

Water photolysis has been studied in liquid phase using neutral aqueous suspensions of $RuO_x/Pt/TiO_2$ particles and UV light. The role played by oxygen in catalyst activity was marked [48].

An inexpensive method of forming monolithic porous titania glass has been reported, as well as some properties that make it uniquely suited to photocatalytic applications, such as its inexpensive fabrication, its high surface area, and its spontaneous photoformation of hydrogen from water without the need for precious metals [49–51].

2.5. *Photoelectrochemical processes*

Research area of photoelectrochemical cells has grown extensively over recent years. The temperature dependency of the resistance and photoelectrochemical properties of

the superconducting samples of Y–Ba–Cu–O and Bi–Sr–Ca–Cu–O doped with different legands have been investigated [52]. Silicon and gallium photoelectrodes have been investigated for solar hydrogen production [53–54].

Very interesting aspects of solar hydrogen production from hydrogen sulfide using semiconductor powders have recently been reported [55]. Haematite and magnetite-based coating obtained by thermal oxidation of conversion coatings could be used as photoanodes [56]. Photoelectrochemical semiconductor septum (CdSe/Ti and TiO$_2$/Ti) solar cells in relation to hydrogen production have been found [57]. A major problem of photoelectrodes for hydrogen production is the photo-corrosion of the photoanode surface [58].

In order to develop a clean burning fuel from renewable sources, methanol is a practical option as a possibility for solar hydrogen storage. The electrochemical reduction of CO$_2$ to CH$_3$OH is thermodynamically more convenient than hydrogen generation, but this process is kinetically inhibited. The development of new electrocatalysts shows that the overvoltage of this reaction could be minimized [59].

Direct conversion of solar energy into hydrogen as a storable energy carrier can in principle be achieved by photoelectrochemical means. However, despite high conversion efficiencies obtained in wet solar cells for the conversion into electrical energy using reversible redox systems in the electrolyte, the direct splitting of water using visible light has not been achieved yet. Recent progress in understanding and possible ways to overcome the underlying basic problems have been reported. The main task to solve is the modification of the semiconductor/electrolyte interface [60]. In principle more detailed investigations confirm the high quality of the semiconductor/electrolyte interface which is necessary to obtain high conversion efficiencies. High efficiencies have been obtained in laboratory solar cells [61].

2.6. Photobiological processes

Photosynthetic bacteria represent a futuristic approach with appreciable extent of light-conversion efficiency [62]. Whey, a by-product of the milk processing industry, has also been used as the efficient substrate for hydrogen production by photosynthetic bacteria [63]. The sustained hydrogen production by immobilized cells by a strain of Rhodopseudomonas at the expense of potato starch [64] and the insolation of high temperature strains showing significant hydrogen production even up to 45°C have been reported [65]. Four strains of Rhodopseudomonas sp. evolved hydrogen at the expense of potato starch, sugarcane juice and whey in the presence of light (2klx)—anaerobic condition (argon/CO$_2$, 95/5, v/v). Among the three substrates, sugarcane juice supported the maximum level of hydrogen production followed by potato starch and whey at the rates of 45, 30 and 25 ml H$_2$ h^{-1} mg^{-1} bacterial cell dry wt, respectively [66].

Hydrogen production is catalyzed by nitrogenase or by the reversible hydrogenase. The functioning of nitrogenase, as well as hydrogenase, is linked to cyanobacteria with the utilization of the products of photosynthetic reactions that generate reductants from water. Thus, it is possible to design bioreactors in which solar energy could be used to produce hydrogen from water with cyanobacteria as biocatalysts [67]. It is

of interest to investigate other conditions for hydrogen production that are cheaper and more convenient for practical bioreactors than hydrogen formation under an argon atmosphere. Molecular hydrogen production by nitrogen-fixing cyanobacteria *Anaebaena variabilis* and *Nostoc muscorum* has been induced by a partial vacuum. A laboratory scale hollow fiber photobioreactor has been assembled for continuous production of hydrogen by immobilized cyanobacterium *A. variabilis* under a partial vacuum. The hollow fibers were composed of semi-permeable polymeric membranes [68]. The bioreactors were designed to allow free movement of small molecular weight nutrients, gases and waste products between the outer surface of the fibers and the inner space (lumen) of the fibers. The cells, due to their large size, are situated on the outer surface of the fibers. All these features are very helpful for the separation and concentration of the products from cell cultures. Another important advantage of the use of hollow fibers for bioreactors is the large surface-to-volume ratio, which allows the design of compact systems. In addition, the photosynthetic activity and hydrogen production are stabilized by immobilization of the cells on solid surfaces. Photo-production of hydrogen by the nitrogen-fixing cyanobacteria *A. variabilis* and *N. muscorum* has been induced by a partial vacuum. A laboratory scale photobioreactor has been designed so that the cyanobacterial growth medium passes from the outside of the fibers into the inner lumen space. Photoproduction of hydrogen at rates 0.002–0.2 ml H_2 mg^{-1} dry wt h^{-1} of cyanobacterial biomass have been observed. The photobioreactors were run for five months with continuous production of hydrogen [69]. Hydrogen production using micro-organisms in hollow fiber bioreactors has been investigated [70].

3. Conclusions

There is important progress in hydrogen production areas, especially in hydrogen production from renewable energy sources. However, more research and development efforts are required for developing hydrogen production methods for commercialization.

References

[1] Veziroğlu TN. International Journal of Hydrogen Energy 1987;12:99.
[2] Winter CJ. International Journal of Hydrogen Energy 1987;12:521.
[3] Serpone N, Lawless D, Terzian R. Solar Energy 1992;49:221.
[4] Bockris JO'M, Dandapani B, Cocke D, Ghoroghchian J. International Journal of Hydrogen Energy 1985;10:179.
[5] Okken PA. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 1723.
[6] Zweig RM. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 1995.
[7] Winter CJ. Proceedings of the Second World Renewable Energy Congress. Reading (England), 1992. p. 91.

[8] Winter CJ, Nitsch J. Hydrogen as an energy carrier. Berlin: Springer, 1988.

[9] Gretz J. Proceedings of the Second World Renewable Energy Congress. Reading (England), 1992. p. 2438.

[10] Block DL, Veziroğlu TN. Proceedings of the Tenth World Hydrogen Energy Conference. Cocoa Beach (Florida, U.S.A.), 1994. Foreword.

[11] Bolton JR. Solar Energy 1996;57(1):37.

[12] Karim AG, Zhou G. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 35.

[13] Rosen MA, Scott DS. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 457.

[14] Linkous CA. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 419.

[15] Kainthla RC, Khan SUM, Bockris JO. International Journal of Hydrogen Energy 1987;12:381.

[16] Vijh AK, Belanger G, Jacques R. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 385.

[17] Rausch S, Wendt H. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 365.

[18] Pushpavanam S, Pushpavanam M, Natarajan SR, Narasimhan KC, Chinnasamy S. International Journal of Hydrogen Energy 1993;18:277.

[19] Gonzalez ER, Avaca LA, Tremiliosi-Filho G, Machado SAS, Ferreira M. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 375.

[20] Savadogo O, Carrier F, Forget E. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 495.

[21] Andolfatto F, Durand R, Michas A, Millet P, Stevens P. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 429.

[22] Stucki S, Boesch D, Schuler A, Constantinescu M. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 309.

[23] Sim K-Y, Son Y-M, Kim J-W. International Journal of Hydrogen Energy 1993;18:287.

[24] Bernhauser C, Knoche KF. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 103.

[25] Lundberg M. International Journal of Hydrogen Energy 1993;18:369.

[26] Yoshida K, Kameyama H, et al. International Journal of Hydrogen Energy 1990;15:171.

[27] Amir R, Sato T, et al. Proceedings of the Eighth World Hydrogen Energy Conference. Honolulu (Hawaii), 1990.

[28] Aihara M, Sakurai M, et al. Proceedings of the Eighth World Hydrogen Energy Conference. Honolulu (Hawaii), 1990.

[29] Amir R, Shuzaki S, Jamamoto K, Kabe T, Kameyama H. International Journal of Hydrogen Energy 1993;18:283.

[30] Onstott E. Journal of Physical Chemistry 1991;95:2520.

[31] Cheng-lin P, Jie Y, Weimen G, Long Z, Jun P. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 271.

[32] Momirlan M. Proceedings of the Second World Renewable Energy Congress. Reading (England), 1992. p. 2588.

[33] Momirlan M. Revue Romaine de Chimie 1992;37:1001.

[34] Momirlan M. Revue Romaine de Chimie 1992;37:205.

[35] Vilcu R, Oancea D, Coseac T, Staicu L. Revue Romaine de Chimie 1992;37:1359.

[36] Vilcu R, Coseac T, Oancea D. Revue Romaine de Chimie 1992;37:651.

[37] Bockris JO'M, Dandapani B, Was JC. In: Böer KW, editor. Advances in solar energy. New York: Plenum Press, 1989. p. 171.

[38] Badescu V. Proceedings of the Second World Renewable Energy Congress. Reading (England), 1992. p. 2716.

[39] Bauer R, Werner HAF. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 623.

[40] Maruthamutu P, Gurunathan K, Subramanian E, Sastri MVC. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 565.

[41] Curco D, Cervera-March S. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 631.

[42] Anpo M, Negishi N, Nishiguchi H. Critical Reviews in Surface Chemistry 1993;3(2):131.

[43] Anpo M, Tomonari M, Fox MA. Journal of Physical Chemistry 1989;93:7300.

[44] Karakitsou KE, Verykios XE. Journal of Physical Chemistry 1993;97:1184.

[45] Holroyd RA, Bielschi BH. Journal of the American Chemical Society 1978;5796.

[46] Gratzel MA. Energy resources through photochemistry and catalysis. New York: Academic Press Inc, 1993.

[47] Sayama K, Arakawa H. Chemistry Letters 1992;253.

[48] Simarro R, Cervera-March S, Esplugas S. International Journal of Hydrogen Energy 1985;10:221.

[49] Kruczynski L, Gesser HD, Turner CW, Speers E. Nature 1981;291:399.

[50] Gesser HD, Kruczynski L, Young YS. Journal of Colloid and Interface Science 1990;135:1.

[51] Gesser HD, Kruczynski L. Journal of Physical Chemistry 1984;88:2751.

[52] Sarkissyan AG, Putnyn EV, Arakelian VM, Aroutinian VM, Begoian KH. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 591.

[53] Specht M. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 527.

[54] Getoff N, Li G, Stockenhuber M, Kotchev K. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 537.

[55] Linkous CA, Mingo TE, Muradov NZ. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 545.

[56] Traverse JP, Organista M, Aries L, Komla A. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 667.

[57] Chandra Babn KS, Pandey RN, Srivastava ON. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 651.

[58] Pong W. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 605.

[59] Bandi A. Journal of the Electrochemical Society 1990;137:2157.

[60] Meissner D. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 517.

[61] Tributsch HD. In: Schiavello, editor. New trends and applications of photocatalysis and photochemistry for environmental problems. Dordrecht: Reidel, 1988. p. 297.

[62] Miyake J, Kawamura S. International Journal of Hydrogen Energy 1987;12:147.

[63] Venkataraman C, Vatsala IM. Proceedings of the Eighth World Hydrogen Energy Conference. Honolulu (Hawaii), 1990. p. 781.

[64] Singh SP. Srivastava SC, Pandey KD. International Journal of Hydrogen Energy 1990;403.

[65] Singh SP, Srivastava SC. International Journal of Hydrogen Energy 1990;403.

[66] Singh SP, Srivastava SC, Pandey KD. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 615.

[67] Hall DO, Rao KK. Chimicaoggi 1989;7:40.

[68] Bunch AW. Journal of Microbiological Methods 1988;8:103.

[69] Markov SA, Krishna Rao K, Hall DO. Proceedings of the Ninth World Hydrogen Energy Conference. Paris (France), 1992. p. 641.

[70] Markov SA, Weaver P, Seibert M. Proceedings of the Eleventh World Hydrogen Energy Conference. Stuttgart (Germany), 1996. p. 2619.